

Oxidized Gold as an Ultrathin Etch Resist Applied in Microcontact Printing

Ruben B. A. Sharpe,[†] Dirk Burdinski,^{*,‡,⊥} Jurriaan Huskens,^{*,†,‡,§} Harold J. W. Zandvliet,^{*,†,||}
David N. Reinhoudt,^{†,§} and Bene Poelsema^{†,||}

MESA+ Institute for Nanotechnology, MESA+ Strategic Research Orientation "Nanofabrication",
Molecular Nanofabrication, and Solid State Physics, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands, and Philips Research, High Tech Campus Eindhoven 11,
5656 AE Eindhoven, The Netherlands

Received July 24, 2006; E-mail: j.huskens@utwente.nl; h.j.w.zandvliet@utwente.nl; dirk.burdinski@philips.com

In this report it is described how a gold surface can be treated with an oxygen plasma to become an effective etch mask. The barrier is expected to be less sensitive to defects than traditional self-assembled monolayer (SAM) barriers and, contrary to these conventional barriers, is expected to spontaneously deteriorate in time.¹ Using a novel patterning scheme based upon microcontact printing (μ CP) of a reductant ink, patterns can be created that can be selectively etched (Figure 1).² Such a scheme offers advantages similar to those of positive microcontact printing ((+) μ CP).³

In μ CP, functional molecules (ink) are transferred to a substrate upon contact with an inked, micropatterned, polymeric stamp. The most widespread application of μ CP is that of patterning dense and highly ordered SAMs of alkanethiols on coinage metals. These monolayers are known to be stable in and shield the underlying surface against various etching solutions.^{2,4} A primary interest in the patterning of SAMs is, therefore, their use as etch masks for the generation of microstructures in the electronics or related industries.^{5,6} The etch-resistant properties of these alkanethiol SAMs are based on steric hindrance and their wettability properties. Their alkyl chains are hydrophobic, and because of their dense packing, they shield the underlying substrate from aqueous solutions. For monolayers, however, there is no averaging of properties in the direction perpendicular to the surface, and therefore such resists are very sensitive to local imperfections in the monolayer packing.¹ Another disadvantage of SAMs as etch resists is that, as with any resist, SAMs remain after etching and have to be stripped from the substrate before further processing.

A standard etch bath consists of an oxidizing agent as well as a ligand to reduce the redox potential of the metal and to solubilize the oxidation product. For the transfer of alkanethiol-protected patterns into a gold substrate, typically thiosulfate is used as the ligand, and ferricyanide, as the oxidant.² Etching therefore calls for negatively charged species to approach the surface (Figure 1). Since many metal oxides are negatively charged in an alkaline, aqueous environment, a thin gold-oxide film was expected to constitute an electrostatic barrier that may significantly inhibit etching (Figure 1b). The etch-protective properties of such an oxide film that consists of multiple atomic layers will be relatively insensitive to defects in any single one of the constituting layers. This insensitivity may be expected to be further enhanced because of the spatial extent of electrostatic screening. Stripping of the gold-oxide film will generally not be necessary because gold oxide is thermodynamically unstable and will spontaneously deteriorate

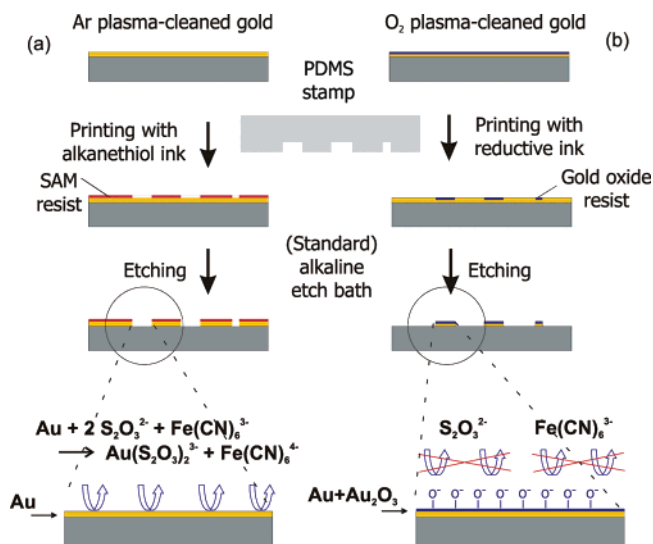


Figure 1. Scheme for patterning of gold using traditional μ CP with a protective SAM ink (a) contrasted against a scheme for the use of oxidized gold as a local etch mask (b). In this second scheme a negatively charged gold-oxide layer inhibits the approach of, also negatively charged, oxidants and ligands and therefore acts as an etch barrier.

within a relatively short time.^{7,8} The versatility of the barrier is furthermore enhanced because oxidized gold can be used as a platform for further chemical functionalization.⁹

The feasibility of this approach depends on several aspects. The oxidized gold needs to be sufficiently stable to allow characterization and postprocessing. This was accomplished by introducing oxygen into the surface of gold substrates using a microwave oxygen plasma.¹⁰ With this method a gold oxide film could be created with a sufficient thickness for the desired stability. It was found that gold exposure to a 300 W, 0.25 mbar O₂ plasma yields a film thickness of ~ 2 nm as determined using spectroscopic ellipsometry. This film thickness, which translates to ~ 10 atomic monolayers of a Au₂O₃ crystal,^{7,8} was found to be relatively insensitive to plasma exposure times in excess of 1 min. In ambient conditions, such a film proved to be stable for several hours, whereas no oxidized gold could be detected upon a thus treated substrate, which had subsequently been submersed for 1 h in a 0.1 M ethanolic solution of triphenylphosphine (TPP). The latter demonstrates the easy removal of the oxide film.

The proposed inhibited rate of etching was demonstrated by comparing the time that was needed to completely dissolve the gold from non-treated substrates with that needed for etching substrates that had been plasma treated prior to etching. Non-treated substrates with a 20 nm gold film were completely stripped within 10 min in a thiosulfate-based etch bath. Uniformly oxidized gold, however,

[†] MESA+ Institute for Nanotechnology, University of Twente.

[‡] MESA+ Strategic Research Orientation "Nanofabrication", University of Twente.

[§] Supramolecular Chemistry and Technology & Molecular Nanofabrication groups, University of Twente.

^{||} Solid State Physics, University of Twente.

[⊥] Philips Research.

only started to show signs of deterioration after an hour of submersion in the etch bath. As a control, an alternative etch bath, consisting of thiourea as the ligand and iron(III)sulfate as oxidant, was also applied to oxidized gold samples. Etching, using this alternative etch bath, does not call for negatively charged species to approach the substrate. Moreover, the etch bath is acidic (pH 2), and therefore, the oxidized gold substrate is not expected to be charged. Using this etch bath, both nontreated and oxidized gold substrates were completely stripped within 2 min. The difference in etch rate of oxidized gold in the two etch baths cannot be explained in terms of a difference in redox potential of the reagents, since the gold is already oxidized. This strongly supports the hypothesis of electrostatic repulsion as an important factor in the etch inhibition of oxidized gold.

Critical to the applicability of this etch protection scheme for patterning is the availability of a convenient route for the creation of a patterned barrier layer. Creating such a pattern entails either the *local oxidation* of a uniform nontreated gold surface or the *local reduction* of a uniformly oxidized surface. Feasible patterning techniques therefore include, e.g., scanning probe lithography (SPL),¹¹ laser-induced local decomposition of gold oxide,¹⁰ parallel field-induced oxidation,¹² reaction through a contact mask,¹³ or reactive μ CP.¹⁴ The latter system (reactive μ CP) was chosen to demonstrate a proof of concept. Because harsh conditions are typically required for the oxidation of gold, with uncertain stability of the oxidized gold as a result, patterning was chosen to be effected via local reduction of oxidized gold. From electrochemical and optical studies it is known that the rate of formation for the first two atomic monolayers of Au_2O_3 is by far the fastest.⁸ This indicates that although chemical reduction is interface bound, it may still have a pronounced effect in the overall rate of decomposition of the oxide film. The formulation of a convenient reactive ink, however, remains nontrivial. We have evaluated neat ethanol and ethanolic solutions of ascorbic acid (AA, saturated), dithiothreitol (DTT, 10 mM), and TPP (0.1 M), as well as solutions of DTT (10 mM) and TPP (0.1 M) in toluene for their use as a reactive ink.

Neat ethanol showed little reactivity when applied from a poly-(dimethylsiloxane) stamp. Etch inhibition remained uniform when a contact time of 15 s was employed, whereas upon 1 min of contact time etch inhibition was found to be uniformly lifted. The latter was also observed upon printing for 15 s with an AA-loaded stamp. Printing of ethanolic solutions of DTT and TPP, however, resulted in clear etch contrast although the transferred pattern was markedly enlarged with respect to the nominal stamp pattern size. In order to limit the contribution of solvent assisted transport of the reactants across the hydrophilic oxidized surface DTT and TPP were also printed from a toluene solution. When sufficient time was allowed for the evaporation of toluene, this greatly improved the area selectivity, with the best results for an ink consisting of 10 mM DTT (Figure 2).

These experiments show the feasibility of a patterning scheme based upon a combination of oxidized gold etch barriers and reactive μ CP. A film of only 10 atomic monolayers of oxidized gold, created using an oxygen plasma, proved to be sufficiently stable for further processing. The barrier properties are ascribed to electrostatic screening, which has several advantages over traditional SAM barriers. An important consideration in the selection of a reactive ink is the requirement that the reactivity of the ink and its tendency for spreading must be matched so that the extent of spreading is low on the time scale of the reaction, as exemplified here for DTT.

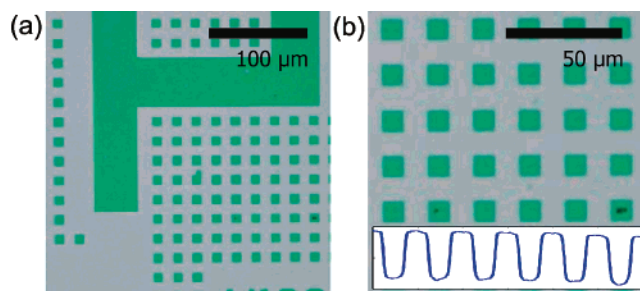


Figure 2. Optical micrographs of an etched sample after local reduction of the oxidized gold barrier using 10 mM DTT in toluene and a contact time of 15 s. The etch time was \sim 30 min. Contrast in etch inhibition was established for areas with widths of over 100 μm as well as for areas with widths as small as 10 μm (a). Panel (b) shows a blowup of a random area from (a), which shows the very good edge definition of the patterns. The insert in panel (b) shows an average intensity profile across the etched squares. The average feature size of these squares was found to be $9.3 \pm 0.1 \mu\text{m}$, whereas the nominal contact area of the corresponding stamp pattern was 10 μm .

In conclusion, we have introduced a new scheme for creating patterned gold substrates, making use of the etch-resistant properties of oxidized gold. Future developments may lead to a reduction process that can be performed without ink spreading, allowing the extension to (far) submicron pattern replication.

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Supporting Information Available: Experimental details and ellipsometry procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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